GB769220

Title:
Polyglycol terephthalates

Abstract:
In the manufacture of filament-forming phthalate polyglycol terephthalates by heating a glycol ester of terephthalic acid in presence of a metal-containing polymerization catalyst, colour formation is inhibited by effecting polymerization in presence of a phosphoric acid, an alkyl phosphate, a hydroxyalkyl phosphate or an aryl phosphate. The glycol ester is preferably made by heating a dialkyl terephthalate with the glycol in presence of an ester-interchange catalyst. Specified glycols are those of formula OH (CH2)nOH where n=2-10 and polyethylene glycols of molecular weight 106-6000. Part of the terephthalic acid may be replaced by isophthalic, hexahydroterephthalic, tribenzoic, adipic, azelaic, naphthalic or 2.5-dimethylterephthalic acids or by bis-p-carboxyphenoxyethane. In examples, dimethyl terephthalate and ethylene glycol were heated in presence of a catalyst and after no more methanol was evolved the glycol terephthalate was added to a polymerization vessel, the phosphorus compound added and the whole heated under reduced pressure, the catalyst combination being (1) zinc acetate, tetraisopropyl titanate and tri-(2-hydroxyethyl) phosphate. (2) Magnesium acetate, antimony trioxid and trihexyl phosphate. (3) Zinc acetate, lithium hydride, antimony trioxide and trihexyl phosphate. (4) Lithium hydride, lead monoxide and triphenyl phosphate. (5) Magnesium formate, lead monoxide, antimony trioxide and tributyl phosphate. (6) Lanthanum acetate, antimony trioxide and phosphoric acid or triethyl phosphate. (7) Manganous acetate, antimony trioxide and tricresyl phosphate or phosphoric acid. (8) Calcium acetate monohydrate and phosphoric acid. (9) Manganous acetate, antimony trioxide and tricresyl phosphate. (10) Zinc acetate dihydrate, tetraisopropyl titanate and tri-(2-hydroxyethyl phosphate). Phosphoric compounds referred to in addition to those exemplified are tri-isopropyl-, triamyl- and tributyl-phosphates; also diphenyl ethyl phosphate, diphenyl phosphate, dibutyl phenyl phosphate, tri-(3-hydroxypropyl) phosphate, dibutyl hydrogen phosphate and phenyl dihydrogen phosphate. Specification 578,079, [Group IV], is referred to.

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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Polyglycol Terephthalates

We, E. I. Du Pont de Nemours and Company, a Corporation organized and existing under the laws of the State of Delaware, United States of America, located at Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved method for the preparation of polymeric esters and more particularly to the preparation of polymeric glycol terephthalates.

A novel class of fiber- and film-forming polymers consisting of polyesters of terephthalic acid and polymethylene glycols containing from 2 to 10 carbon atoms is disclosed in British Patent Specification No. 578,079. A commercially important example of this class is polyethylene terephthalate, which is prepared by carrying out an ester interchange reaction between ethylene glycol and dimethyl terephthalate (DMT) followed by polymerization at elevated temperatures and reduced pressures. In effecting these ester interchange and polymerization reactions various catalytic agents have been employed to accelerate the rate of reaction. However, the use of catalytic systems in polymer preparation has also been attended by the development of color in the polymer, the extent of color formation being dependent on the particular nature of the catalyst. A process for retarding the formation of color during polymerization without seriously impairing catalytic activity would be of great importance in preparing polyethylene terephthalate for many commercial uses, and this applies especially to textile uses, for which colorless or white fibers are greatly desired. Even more desirable is a polymerization in which colorless products are produced at rates even faster than heretofore attained.

An object of this invention is the provision of a process for producing polymeric esters rapidly. A further object is the production in a rapid manner of such esters which are substantially free of color. Other objects appear hereinafter.

The invention consists in a process for the production of polyglycol terephthalates which comprises heating a substantially monomeric glycol ester of terephthalic acid in the presence of a metal-containing polymerization catalyst and a phosphorus compound selected from the group consisting of phosphoric acid, alkyl phosphates, hydroxyalkylphosphates and aryl phosphates under reduced pressure until a filament-forming polymer is produced.

The invention may be carried out by reacting one or more glycols and terephthalic acid or an ester thereof in an esterification or ester interchange reaction to produce a glycol terephthalate. This ester compound is in substantially monomeric form and is exemplified by the reaction product of ethylene glycol and dimethyl terephthalate, namely, bis-(2-hydroxyethyl) terephthalate.

The monomer may be formed by an ester interchange or other esterification reaction. The esterification may be effected in the presence of an esterification catalyst. The esterification and polymerization catalysts may be the same but preferably are different, and, if different, may be added immediately before each respective reaction. If the catalysts are the same, the addition of a single amount of it may occur prior to the first step. In addition to the aforementioned catalysts and in accordance with our invention, the phosphorus compound which modifies the color is added, preferably immediately before the polymerization step, although earlier addition will still effect color modification while perhaps slowing down the esterification reaction.

Polymerization is conducted by heating at elevated temperature under reduced pressure to remove the volatile material produced which is chiefly the glycol used, being ethylene glycol if bis-(2-hydroxyethyl) terephthalate is being polymerized. The modifiers

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of this invention operate with the wide variety of catalysts used in the preparation of glycol terephthalate polymers, and by use of the modifiers of this invention substantially colorless polymers are produced at good reaction rates.

The following examples illustrate the principles and practice of this invention and are given for illustrative purposes only. All parts and percentages are by weight unless otherwise specified.

Example 1

The results of a series of experiments on the preparation of polyethylene terephthalate are recorded in Table I. In each case the reaction was carried out in the following manner: 50 parts of dimethyl terephthalate and 50 parts of ethylene glycol were placed in a flask together with the amount of catalyst indicated in the table (percentages calculated on the basis of anhydrous compounds). The flask was fitted with a condenser and heated at atmospheric pressure, whereupon the mixture began to evolve methanol in the range 160-180°C., the temperature depending on the catalyst and its concentration. Heating was continued at such a rate that continuous gentle ebullition was maintained until no further methanol was evolved, the final pot temperature being about 220°C. in each case. The liquid was then introduced into a polymerization tube together with the indicated amount of modifier, and the mixture was heated at 275°C. under a vacuum of 0.5 to 1.0 mm. of mercury for the indicated length of time. A continuous stream of nitrogen was introduced through a capillary tube to agitate the mixture. At the end of the polymerization period the color of the molten polymer was compared visually with arbitrary color standards consisting of aqueous solutions of du Pont Pontamine Catechu 3 G dye according to the following system of color ratings:

0 = water.
1 = 0.00025 grams of dye per 100 ml of solution.
2 = twice as much dye as 1.
3 = three times as much dye as 1.
4 = four times as much dye as 1.
5 = etc.

This system of color standards was designed as a measure of the yellowish to brown range of colors generally encountered in the preparation of polyethylene terephthalate.

The intrinsic viscosity of the resulting polymer, a measure of the degree of polymerization, was determined in dilute solutions of the polymer in Fomal, which comprises 58.8 parts by weight of phenol and 41.2 parts by weight of trichlorophenol.

Table I.

	Catalyst	Mol %[1]	Modifier	Mol %[1]	Pm.T.[2]	I.V.[3]	Color
1.	Zinc Acetate ..	0.053	None	—	4	0.67	12
	Tetraisopropyl Titanate	0.007					
	Zinc Acetate ..	0.053	Tri-(2-hydroxyethyl) Phosphate	0.076	4	0.65	5
	Tetraisopropyl Titanate	0.007					
2.	Magnesium Acetate	0.24	None	—	2	0.48	2
	Antimony Trioxide	0.020					
	Magnesium Acetate	0.24	Trihexyl phosphate	0.125	2	0.42	1
	Antimony Trioxide	0.020					
3.	Zinc Acetate ..	0.031	None	—	6	0.75	8
	Lithium Hydride ..	0.122					
	Antimony Trioxide	0.020					
	Zinc Acetate ..	0.031	Trihexyl Phosphate	0.061	6	0.72	3
	Lithium Hydride ..	0.122					
	Antimony Trioxide	0.020					
4.	Lithium Hydride ..	0.98	None	—	5	0.35	5
	Lead Monoxide ..	0.017					
	Lithium Hydride ..	0.98	Triphenyl Phosphate	0.06	5	0.41	3-4
	Lead Monoxide ..	0.017					

1. Based on DMT.
2. Polymerization time in hours.
3. Intrinsic Viscosity.

As shown in Table I in every instance when the phosphorus compound of this invention is used the polymer produced has much better color than a polymer produced under the same conditions but in the absence of modifier.

Example 2

Table II given below lists the results obtained in a series of autoclave preparations of polyethylene terephthalate. In each case 58 parts of dimethyl terephthalate, 40 parts of ethylene glycol and the indicated amount of catalyst were introduced into a stainless steel batch still equipped with a stirrer and a condenser. When the mixture was heated methanol was evolved, the reaction requir-

ing from 2.5 to 4 hours depending on the catalyst and its concentration. The resulting material was transferred to a stainless steel autoclave equipped with a stainless steel stirrer, and the modifier was added in the indicated amount. The reaction mixture was heated to 275°C. and the autoclave was evacuated gradually through an ice trap and a dry ice trap to an absolute pressure of about 0.5 mm. of mercury. After polymerization at this full vacuum for the indicated period of time, the polymer was withdrawn and the molten polymer was compared with the previously described arbitrary color standards.

TABLE II.

	Catalyst	Mol %[1]	Modifier	Mol %[1]	Pm.T.[2]	I.V.[3]	Color
1.	Magnesium Formate	0.052	None	—	3	0.63	7
	Lead Monoxide ..	0.009					
	Antimony Trioxide	0.020					
	Magnesium Formate	0.052	Tributyl Phosphate	0.06	5	0.65	4
	Lead Monoxide ..	0.009					
	Antimony Trioxide	0.020					
2.	Lanthanum Acetate	0.023	None	—	5	0.67	4
	Antimony Trioxide	0.020					
	Lanthanum Acetate	0.034	Phosphoric Acid	0.095	6	0.66	2
	Antimony Trioxide	0.033					
	Lanthanum Acetate	0.034	Triethyl Phosphate	0.032	6	0.64	1
	Antimony Trioxide	0.020					
3.	Manganous Acetate	0.040	None	—	4	0.64	9
	Antimony Trioxide	0.020					
	Manganous Acetate	0.040	Tricresyl Phosphate	0.040	8	0.64	1
	Antimony Trioxide	0.020					
	Manganous Acetate	0.040	Phosphoric Acid	0.065	8	0.68	2
	Antimony Trioxide	0.020					

1. Based on DMT.
2. Polymerization time in hours.
3. Intrinsic Viscosity.

Here again, when a modifier of this invention was used, higher quality polymer was obtained. The results in Tables I and II show that phosphoric acid and its esters are useful in producing white or colorless polyethylene terephthalates. Frequently, when some catalyst systems, such as those containing compounds of antimony, lead or arsenic, are used with other additives a grayish cast to the polymer appears. This grayish color is believed to be caused by the reduction of the metallic ions to the metal. A distinct advantage of the modifiers of this invention lies in the fact that there is no such effect, and the polymers produced are entirely free from the grayish color when the phosphoric acid or esters are used with the above-mentioned catalysts.

EXAMPLE 3

Ninety parts of ethylene glycol was heated with 28.1 parts of dimethyl terephthalate and about 0.073 part calcium acetate monohydrate until the theoretical quantity of methanol (9.25 parts) had been removed. The resulting mixture was dissolved in water, heated to 80°C., filtered, and cooled to 50°C., whereupon crystals were obtained. The crystals were filtered off and recrystallized from water twice. Of the resulting catalyst-free bis-(2-hydroxyethyl) terephthalate 4.4 parts was placed in a vapor-jacketed glass vessel equipped with a clean stainless steel stirrer. The ester was heated for 6.5 hours at 283°C. under nitrogen at atmospheric pressure with continuous agitation by the steel stirrer at 100 r.p.m. The resulting liquid had a color of 3 units when compared with the previously described standards. In a second experiment in which 0.14 mol % of phosphoric acid was added to the ester, only 1 unit of color was developed under the same conditions.

Phosphoric acid and its esters also are useful in inhibiting color formation resulting from adventitious catalysis by metallic impurities which might be encountered in commercial practice wherever metallic reaction vessels are used. The surprising ease with which such contamination may occur is illustrated by this example.

In order to obtain the full effect of the modifier, it should be added to the reaction mixture early during the polymerization step, or preferably before polymerization has begun. As shown in the following examples 4 and 5 one function of the inhibitor is to prevent or retard the development of color; when added late in the polymerization step however the inhibitor appears to have little or no effect on color which has already appeared.

EXAMPLE 4

Polyethylene terephthalate was prepared in an autoclave following the procedure of Example 2. The catalyst was 0.062 mol % manganous acetate and 0.027 mol % antimony trioxide; no modifier was used. After 3 hours at full vacuum the polymer had developed 7 units of color as compared with

the color standards, and the intrinsic viscosity was 0.67. In another autoclave run the same catalyst system was used, but 0.060 mol % of tricresyl phosphate was added to the reaction mixture after the ester exchange step and before polymerization had begun. The polymer developed 3 units of color after 4.5 hours at full vacuum, and the intrinsic viscosity was 0.65. In a third experiment the mixture was allowed to polymerize under full vacuum for 2 hours without a modifier; 0.060 mol % of tricresyl phosphate was then added and polymerization under full vacuum was continued for 45 minutes. The color of the molten polymer was 8 units, and the intrinsic viscosity was 0.65.

Although the modifiers of this invention must be added to the reaction mixture before polymerization has proceeded to any great extent, it is not necessary that they be present during the ester exchange step to obtain the desired high quality polymer. In fact, it will generally be desirable to omit the modifier during ester exchange when reaction time is a factor, since phosphorus compounds retard the rate of ester exchange. In commercial practice it is desirable to carry out the ester exchange reaction continuously under essentially constant temperature conditions; in such a continuous process the inhibitory effect of phosphorus compounds on the exchange rate is especially serious since a much larger reaction vessel will be required to maintain a given withdrawal rate of product containing a given low percentage of unreacted dimethyl terephthalate.

EXAMPLE 5

To a flask equipped with a condenser was added 50 parts of dimethyl terephthalate, 50 parts of ethylene glycol, 0.03 part of zinc acetate dihydrate (0.053 mol % based on DMT), and 0.005 part of tetraisopropyl titanate (0.007 mol % based on DMT). The mixture was heated under atmospheric pressure; at 171°C. methanol began to distil over. Heating was continued at such a rate that continuous gentle ebullition was maintained until no further methanol was evolved, the final pot temperature being about 220°C. The reaction required 1.4 hours. The experiment was repeated with the addition to the reaction mixture of 0.045 part of tri-(2-hydroxyethyl) phosphate (0.076 mol % based on DMT). No methanol was evolved until the temperature of the reaction mixture had reached 180°C., and 1.9 hours were required to complete the evolution of methanol.

EXAMPLE 6

The reaction chamber for a constant temperature ester exchange apparatus consisted of a stainless steel beaker, 2 7/8" in diameter and 2 1/4" deep, fitted with a stainless steel cover clamped down with wing nuts and sealed with a gasket prepared from a sheet of polytetrafluoroethylene. The outside of the beaker was electroplated with copper, wound with resistance wire, and insulated. The cover was provided with openings for two thermocouple wells, an inlet tube for a stream of nitrogen gas, and a joint connecting to a column for removal of the methanol. The temperature in the reactor was controlled by a thermocouple acting through a pyrometer controller and the temperature was checked constantly with another thermocouple connected to a potentiometer. The methanol was removed through an electrically heated column equipped with a rotating strip of stainless steel gauze twisted spirally about a vertical shaft; features of this column included good separating efficiency, high throughput rate, and low holdup. The jacket temperature was maintained slightly below the boiling point of methanol (65°C.). After passing through the column, the methanol was condensed and collected.

In each run shown in Table III, a charge of 75 parts of dimethyl terephthalate and about 73 parts of glycol was heated to 175°C., whereupon a preheated slurry of the indicated amount of catalyst in 11 additional parts of glycol was introduced. The temperature of the mixture was maintained at 175° ± 2.5°C. throughout the run, and a continuous stream of nitrogen gas was maintained to aid removal of the methanol. The reaction mixture was stirred slowly by a magnetic stirrer in a stainless steel case. The volume of methanol collected after 30, 60 and 120 minutes was recorded and the percentages based on the theoretical yield of methanol are shown in the table.

TABLE III.

Catalyst	Mol % (Based on DMT)	Methanol Recovered (% of theoretical) 30 min.	60 min.	120 min.
1. Manganous Acetate	0.062	83	92	97
Antimony Trioxide	0.020			
Manganous Acetate	0.062	53	77	90
Antimony Trioxide	0.020			
Dibutyl Hydrogen Phosphate	0.059			
2. Manganous Acetate	0.040	68	85	93
Manganous Acetate	0.040	51	69	82
Triethyl Phosphate	0.086			
Manganous Acetate	0.040	No reaction in 75 minutes		
Phosphoric Acid	0.079			

As indicated in the above table there is more unreacted material left after a given time when the modifier is present in the interchange reaction than when it is omitted. Thus, contrary to expectations, a decided advantage is gained when the modifier is added after interchange. The more rapid production of polymer, that is, amount of polymer per unit of time, is an outstanding feature of this invention.

As can be seen from the above examples, the modifiers of this invention are added to a monomeric glycol terephthalate which has an intrinsic viscosity of substantially zero (say 0.0 to 0.15) and the heating of the modified reaction media is continued until the intrinsic viscosity of the resultant polymer is about 0.5 or higher. Vacuum is applied to remove volatile material and to bring polymerization to the desired level.

Among the modifiers that may be used are the triaryl phosphates, such as triphenyl phosphate, and the trialkyl phosphates, such as triethyl phosphate, tri-isopropyl phosphate, triamyl phosphate, tributyl phosphate and trihexyl phosphate. Still others include diphenyl ethyl phosphate, diphenyl phosphate and dibutyl phenyl phosphate. Glycol esters of phosphoric acid, such as tri-(2-hydroxyethyl) phosphate and tri(3-hydroxypropyl) phosphate are especially useful additives. Partially esterified phosphoric acids, such as dibutyl hydrogen phosphate and phenyl dihydrogen phosphate also are very useful. Phosphoric acid itself may be added in the form of orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid or in other forms differing in degree of hydration. One advantage of the modifiers of this invention lies in their chemical simplicity. Complicated structures are not involved. In fact it is preferred to use modifiers which do not contain nitrogen or halogen atoms such as chlorine. The modifiers of this invention are inexpensive and readily available.

Further, they are very effective and only small amounts need be used. The amount of the phosphoric acid or phosphate ester added will depend in part on the amount of catalyst used. Usually it will be desirable to use an amount in the range of about 0.05 to about 2.0 mols of modifier for each mol of catalyst, based on the total number of mols of all catalysts if more than one catalyst is used. If less than 0.05 mol is used, the effect is very small. On the other hand, the addition in excess of 2 mols will produce little additional advantage.

The phosphate modifiers employed in this invention can be used with any of the well-known catalysts or catalyst combinations effective in the preparation of the polyesters. In practical applications a system of two or more catalysts will generally be used containing one or more components especially effective in promoting the ester exchange reaction between ethylene glycol and dimethyl terephthalate together with one or more additional components which are effective in promoting the polymerization of the monomeric glycol terephthalate. Examples of catalytic materials useful in the ester exchange reaction include the alkali metals and their hydrides and compounds of certain metals, such as calcium, magnesium, lanthanum, manganese, and cobalt. Many of these catalysts also are effective in the initial stages of polymerization, but it will usually be desirable to add a specific polymerization catalyst such as antimony trioxide. Esters of titanium can also be used to catalyze the polymerization reaction. Usually the polymerization catalyst will not retard the rate of ester exchange, and where this is the case it is generally convenient to add all of the catalysts at the beginning of the reaction.

Associated with each catalyst system is a secondary catalytic effect on the reactions of color-forming bodies in the reaction mixture. It is the function of the phosphate additives of this invention to inhibit this secondary catalytic effect without seriously retarding the ability of the catalysts to function in the polymerization reaction. When the tendency of a given catalyst to produce color is high, the phosphate modifiers of this invention will usually operate to reduce the color to acceptable levels. When a catalyst having an inherently low color-forming effect is used, a still further reduction in polymer color is achieved.

Phosphoric acid and the various phosphate esters are substantially equivalent on a molar basis with regard to the inhibition of color. Mixtures of two or more of the phosphate inhibitors are effective to an extent roughly proportional to the total molar quantities used. In using the more volatile members of the group it will frequently be desirable to delay the application of vacuum to the reaction system to allow ester interchange with the glycol to take place. In processes in which the excess glycol is to be recovered and reused, it may be desirable to avoid the use of aryl esters of phosphoric acid. Phenols evolved from these compounds are carried over into the glycol recovery system and are very difficult to remove from the glycol by distillation or other common industrial purification methods. Accumulated phenols would have a deleterious effect on the ester exchange reaction rate.

In commercial applications, it is desirable to combine the recovered glycol with fresh ethylene glycol as new starting material for the reaction; however, ethylene glycol containing phenols as impurities is unsatisfactory because phenols have a deleterious effect on the ester exchange reaction rate. After several cycles, the accumulated phenols build

up to intolerably high levels.

Although the process and advantages of the present invention have been particularly described with respect to the preparation of polyethylene terephthalate from dimethyl terephthalate, it should be understood that the invention is fully applicable to the polymerization of bis-(2-hydroxyethyl) terephthalate derived from whatever source and includes the preparation of modified polyethylene terephthalates, i.e., modified with small quantities, e.g., up to 20 mol % based on the terephthalate content of the polyester of other dicarboxylic acids. For example, glycol, terephthalic acid, or a dialkyl ester thereof, and a second acid or ester thereof, may be reacted together to form a copolyester, the second acid being selected from the group consisting of isophthalic acid, bibenzoic acid, hexahydro terephthalic acid, adipic acid, sebacic acid, azelaic acid, the naphthalic acids, 2,5-dimethyl terephthalic acid, and bis-p-carboxyphenoxyethane.

It is also within the scope of the present invention to prepare polyesters by reacting other glycols besides ethylene glycol, such glycols being selected from the series $HO(CH_2)_nOH$ where "n" is an integer from 2 to 10 inclusive. Polyethylene glycols having molecular weights of about 106 to about 6,000 may also be used in polymer preparation. And, in place of dimethyl terephthalate, there may be employed as monomer any of the terephthalic esters of saturated aliphatic monohydric alcohols containing up to and including 7 carbon atoms.

The products produced by the novel process of this invention are highly desirable. They are color-free polymers which may be readily shaped into films and fibers by conventional spinning techniques, such as by melt spinning. The conditions of polymer preparation and shaping are described in the prior art. For example, such techniques are disclosed in British Patent Specification No. 578,079 and U.S. Patent Nos. 2,534,028, 2,641,592 and 2,647,885 among others.

What we claim is:—

1. A process for the production of polyglycol terephthalates which comprises heating a substantially monomeric glycol ester of terephthalic acid in the presence of a metal-containing polymerization catalyst and a phosphorus compound selected from the group consisting of phosphoric acid, alkyl phosphates, hydroxyalkylphosphates and aryl phosphates under reduced pressure until a filament-forming polymer is produced.

2. The process as claimed in Claim 1 wherein the monomer is formed by reacting one or more glycols with terephthalic acid or an ester or other ester forming derivative thereof.

3. The process as claimed in Claim 2 wherein the monomer forming reaction takes place in the presence of an esterification catalyst.

4. A process as claimed in any of the preceding claims wherein there is present in the reaction mixture a small quantity up to 20 mol % based on the terephthalate content of the polyester of other carboxylic acids or esters thereof selected from the group consisting of isophthalic acid, hexahydroterephthalic acid, bibenzoic acid, adipic acid, sebacic acid, azelaic acid, the naphthalic acids, 2,5-dimethyl terephthalic acid and bis-p-carboxyphenoxyethane.

5. A process in accordance with any of the preceding claims wherein said monomeric glycol ester is bis-(2-hydroxyethyl) terephthalate.

6. A process in accordance with any of the preceding claims in which the amount of the phosphorus compound is from about 0.05 to about 2.0 mols per pol of polymerization catalyst present.

7. A process in accordance with Claim 6 in which the said monomeric ester has an intrinsic viscosity of substantially zero.

8. A process in accordance with Claim 6 in which the said heating is continued until the said polymer has an intrinsic viscosity of at least about 0.5.

9. A process in accordance with any of the preceding Claims 2 to 8 in which the terephthalic acid ester employed in the esterification reaction is dimethyl terephthalate.

10. A process in accordance with Claim 9 in which said glycol is ethylene glycol.

11. A process for the production of polyglycol terephthalates substantially as hereinbefore described.

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